

X-ray scattering studies of structural changes in swollen macromolecular networks after abrupt temperature changes

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Introduction

Hydrogel-polymer networks swollen in water are soft and gentle materials that are now beginning to replace some hard materials in various applications. Polyelectrolyte hydrogels carry charged groups, and the charges considerably affect their structure and properties. Various external stimuli, such as changes in temperature, electric field, pH, etc., can control gel swelling (volume). Such gels belong to the group of responsive gels. Particularly, first order (collapse) volume phase transition in hydrogels induced by a change of temperature is of a great importance in applications [1].

At collapse, the volume of the gel changes from 10 to 1000 times from expanded state (at low temperatures) to collapsed state (at high temperatures). After a sudden temperature increase (due to polymer-water incompatibility), a microphase separation of water in swollen gel appears. This leads to the formation of a heterogeneous structure and affects the mechanical and optical properties of the gels [1, 2]. While the mechanical properties are mostly influenced by swollen gel matrix, the optical properties are influenced mostly by droplets of excluded phase. Studies using small-angle scattering by neutrons and x-rays have been performed and have played an important role in the research on these heterogeneous structures [2–4]. The use of ultrasmall-angle x-ray scattering (USAXS) since it is sensitive to larger features can provide novel information in this field as it bridges a gap in the size ranges of features studied by traditional small-angle scattering cameras and light scattering.

Methods and Materials

The USAXS instrument at 33-ID-D is a Bonse-Hart camera similar to the one described in [5]. The Q range that can be studied is 0.00015 to 0.1 Å⁻¹. The measurement time of this camera to obtain a spectrum in this Q range is routinely about 17 minutes.

A heater was designed to allow *in situ* measurement of liquid and gel materials at various temperatures. As tested, the heater can be safely operated between room temperature and 100°C. In the current experiment, the samples were heated in the range between room temperature (25°C) and 90°C.

Samples were prepared at the Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic. A series of different water solutions and hydrogels were prepared from isopropylacrylamide (series IPPAm), polyvinylmethylether (PVME), and poly(N,N-diethylacrylamide) (PDEAAm); each series contained varying numbers of samples. While linear polymers (from which

solutions were made) were prepared from corresponding monomers, networks were polymerized from monomers in the presence of crosslinker; in both cases, samples were obtained with or without charges on the chains. These were introduced by charged co-monomers of various structures. More detailed descriptions can be found elsewhere [1, 6, 7].

Samples were measured at room temperature and after an abrupt increase in temperature. At least four temperature jumps were measured for each sample and a maximum temperature was selected so that the sample was in collapsed state (or at the maximum operating temperature of the heater). The PDEAAm sample (with crosslinker and no charges) was also selected for an aging study during which the sample was heated to 35°C and measured repeatedly for about 12 hours to obtain the time dependence of the structure at this temperature.

Results

While the detailed evaluation of the results is still ongoing, the preliminary data showed significant differences between the scattering from samples even within one series. Generally, samples without charge collapse at lower temperatures, and in some cases, the samples with charge did not collapse at all in the temperature region studied. Furthermore, significant differences were found between the different series. An IPPAm sample without charge showed formation of structure with Guinier radius about 100 Å at 33°C and 37°C. However, this structure disappeared at 45°C and was replaced by structure with large sizes, since the scattering at this temperature was nearly all Porod scattering from Q about 0.0005 Å⁻¹ higher. The PVME sample with no charge showed formation of structure with Guinier radius about 150 Å between 33°C and 37°C that at 45°C grew in size to about 500 Å and grew in intensity. Presence of large feature structure cannot be reliably distinguished from these measurements, even though it is likely to exist. And finally, the PDEAAm sample seemed to exhibit behavior almost like a combination of both IPPAm and PVME.

The aged PDEAAm sample first showed formation of the structure observed during the temperature-dependent studies, which grew in size out of the studied Q range within about an hour. After that, mostly Porod tail over all of the Q range studied was observed. The scattering from the sample at higher aging times (four hours) reduced even further, consistent with an increase in the sizes of or a decrease in the volume of the scattering features. Since the sample volume decreased significantly, disappearance of the scattering features is very likely.

Discussion

Significant variations in structure of the studied polymers were found using USAXS measurements. The results are now being evaluated and will be related to the chemistry of these gels as well as to their mechanical properties. One major new result obtained with these measurements that was not previously available is the observation of the large feature at small Q range (0.05 to 0.0005 Å⁻¹). These results are leading to an improved insight into collapse of these polymer materials.

Acknowledgments

The UNI-CAT facility at the Advanced Photon Source (APS) is supported by the University of Illinois at Urbana-Champaign (U. S. Department of Energy, the State of Illinois-IBHE-HECA, and the National Science Foundation), the Oak Ridge National Laboratory (U. S. Department of Energy), the National Institute of Standards and Technology (U. S. Department of Commerce), and UOP LLC. The APS is supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

References

- [1] M. Ilavsky, *Adv. Polym. Sci.* **109**, 173 (1993).
- [2] J. Plestil, M. Ilavsky, *et. al.*, *Polymer* **34** (23), 4846 (1993).
- [3] W. Wu and M. Shibayama, *et al.*, *Macromolecules* **22**, 2245 (1990).
- [4] E. Geissler and S. Horkay, *et. al.*, *Macromolecules* **24**, 6006 (1991).
- [5] *J. Appl. Cryst.* **24**, 30–37 (1991).
- [6] G. Mamytbekov, K. Bouchal, *et. al.*, *Europ. Polymer J.* **35**, 1925 (1999).
- [7] M. Ilavsky, G. Mamytbekov, *et. al.*, *Polymer Bulletin* **43**, 109 (1999).